ELECTRONIC SUPPORTING INFORMATION

Counterion-dependent deuteration of pentamethylcyclopentadiene in water-soluble cationic Rh(III) complexes assisted by PTA.

[a] Dipartimento di Chimica, Università di Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy.

[b] Departamento de Química Inorgánica, Universidade de Vigo, Campus Universitario, E-36310 Vigo, Spain.

[c] ICCOM-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy.

Experimental Details

General procedures, methods and materials

All solvents were purified by conventional procedures[1] and distilled prior to use. PTA,[2] THP,[3] $[Cp^*RhCl_2]_2$,[4] $[Cp^*RhCl_2(PTA)]$,[5] $[Cp^*RhCl(PTA)_2]Cl$ (**1**Cl),[5] $[Cp^*Rh(H_2O)_3](OTf)_2$,[6] $[Cp^*IrCl(PTA)_2]Cl$ (**2**Cl),[7] $[Cp^*RuCl(PTA)_2]$,[8] $[Cp^*RhCl(THP)_2]$ and $[Cp^*RhCl(THP)(PTA)]$[9] were prepared according to published methods. Other reagents were purchased from commercial sources in the highest available purity and used as received. NMR spectra [^1H, ^{19}F, $^{31}P\{^1H\}$] were obtained with a Bruker ARX-400 spectrometer operating at frequencies of 400, 376 and 161 MHz, respectively; ^1H NMR signals were referenced to external TMS, those of ^{19}F to $CFCl_3$ and those of $^{31}P\{^1H\}$ to 85% H_3PO_4. Microanalyses were carried out with a Fisons EA-1108 elemental analyser. pH measurements were carried out with a Crison GLP 21+ pH-meter equipped with a pHR-146 micro-combination pH electrode specifically designed for measuring micro samples in the range of 0-12. Buffer solutions of pH 4.01, 7.00, and 9.21 were utilised for calibration. The value of pD has been obtained subtracting 0.44 from the measured values.[10]

Synthesis of [Cp*RhCl(PTA)$_2$]PF$_6$, (1PF$_6$). 95 mg of NBu_4PF_6 (0.24 mmol) in warm methanol (5 mL) were added to a solution of **1**Cl (100 mg, 0.16 mmol) in boiling methanol (10 mL). The system was cooled and the product was obtained as a microcrystalline orange-yellow powder, which was washed with MeOH (5 mL) and Et_2O (10 mL). Yield: 92%. Anal. Calcd for $C_{22}H_{39}N_6ClP_3F_6Rh$: C, 36.06; H, 5.36; N, 11.47. Found: C, 36.12; H, 5.39; N, 11.52.

Synthesis of [Cp*RhCl(PTA)$_2$]OTf, (1OTf). 32 mg of NaOTf (0.18 mmol) in warm methanol (5 mL) were added to a solution of **1**Cl (100 mg, 0.16 mmol) in boiling methanol (10 mL). After the cooling of the system, Et_2O was slowly added, and a yellow product precipitated. This solid was redissolved in CH_2Cl_2, filtered through Celite to remove NaCl and the excess of NaOTf, and precipitated with Et_2O (15 mL). Yield: 85%. Anal. Calcd for $C_{23}H_{39}N_6ClP_2O_3SF_3Rh$: C, 37.49; H, 5.33; N, 11.40. Found: C, 37.52; H, 5.38; N, 11.49.

Synthesis of [Cp*RhCl(PTA)$_2$]BF$_4$, (1BF$_4$). 36 mg of $NaBF_4$ (0.32 mmol) in boiling methanol (5 mL) were added to a solution of **1**Cl (100 mg, 0.16 mmol) in boiling methanol (10 mL). The system was cooled and the product was obtained as a micro-crystalline orange-yellow powder, which was washed with MeOH (5 mL) and Et_2O (10 mL). Yield: 94%. Anal. Calcd for $C_{22}H_{39}N_6BClP_2F_4Rh$: C, 39.16; H, 5.83; N, 12.46. Found: C, 39.12; H, 5.88; N, 12.53.

Synthesis of [Cp*RhCl(PTA)$_2$]I, (1I). 24 mg of NaI (0.16 mmol) in warm methanol (5 mL) were added to a solution of **1**Cl (100 mg, 0.16 mmol) in boiling methanol (10 mL). The system was cooled and the product was obtained as an orange-yellow solid, which was redissolved in CH_2Cl_2, filtered through Celite to remove the NaCl and finally precipitated with Et_2O (10 mL). Yield: 86%. Anal. Calcd for $C_{22}H_{39}N_6ClP_2IRh$: C, 36.97; H, 5.50; N, 11.76. Found: C, 37.01; H, 5.56; N, 11.84.

Synthesis of [Cp*Rh (PTA)$_3$](OTf)$_2$, (3OTf). To a solution of [Cp*Rh(H$_2$O)$_3$]OTf (100 mg, 0.17mmol) in degassed H$_2$O (15 mL), PTA (80 mg, 0.51 mmol) was added and the mixture was stirred for 3 h at room temperature. The yellow solution obtained was concentrated under vacuum to give a yellow solid that was washed with Et$_2$O (15 mL). Yield: 95.0%. Anal. Calc. for $C_{29}H_{51}N_9P_3O_3SF_3Rh$: C, 40.57; H, 5.99; N, 14.68. Found: C, 40.53; H, 5. 92; N, 14.72 %. ^{1}H NMR (D$_2$O): δ 2.17 (q, $^4J_{HP}$ = 3.48 Hz, CpCH$_3$, 15H), 4.47 (br, PCH$_2$N, 18H), 4.60–4.86 (m, NCH$_2$N, 18H) ppm. 31P{1H} NMR (D$_2$O): δ –43.50 (d, $^1J_{PRh}$ = 120.8 Hz) ppm.

Eyring plots

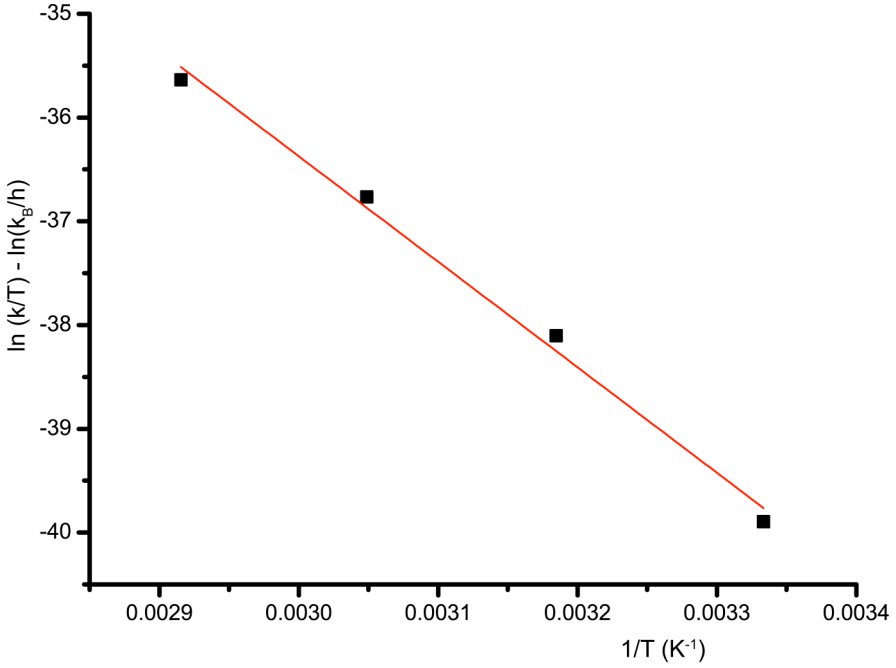

Figure S1. Eyring plot for **1**PF$_6$. The straight red line is the best linear fit, ln k/T – ln k$_B$/h = (-6 ± 2) - (10200 ± 600)/T, r^2 = 0.980.

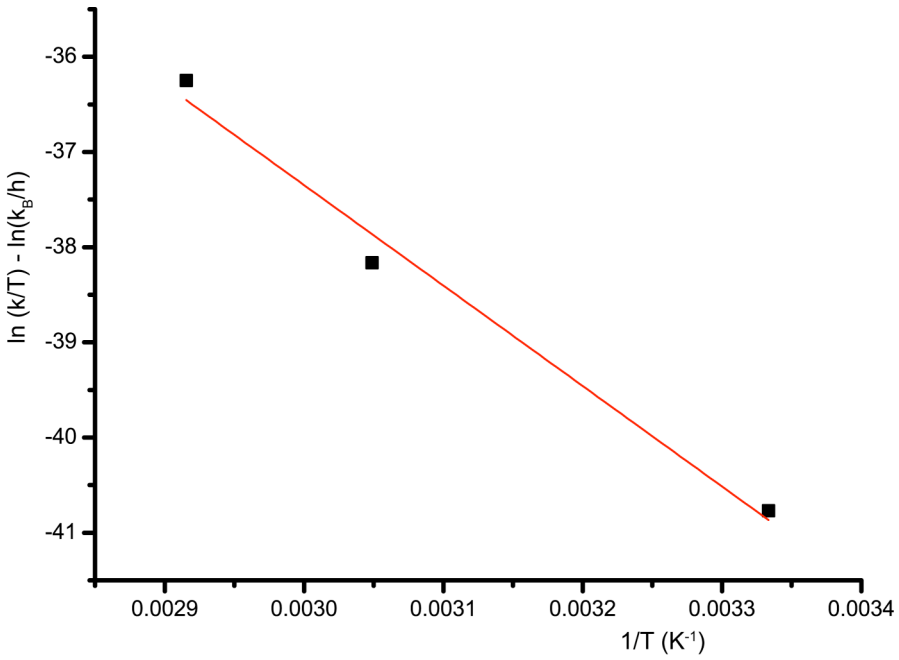

Figure S2. Eyring plot for **1**Cl. The straight red line is the best linear fit, ln k – ln k_B/h = (-6 ± 4) - (11000 ± 1000)/T, r^2 = 0.945.

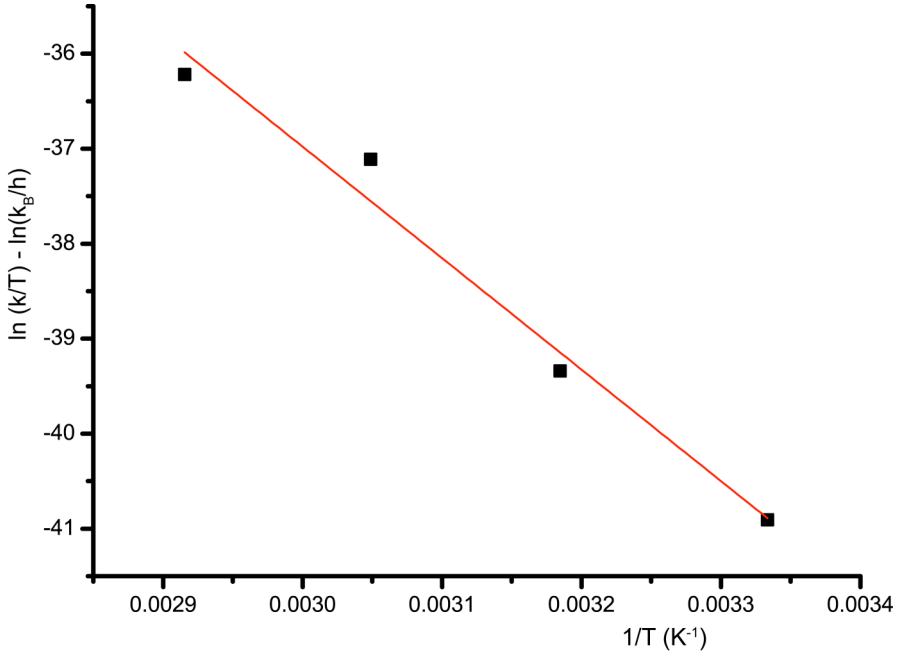

Figure S3. Eyring plot for **4**OTf. The straight red line is the best linear fit, ln k – ln k_B/h = (-2 ± 4) - (12000 ± 1000)/T, r^2 = 0.941.

H/D exchange kinetic measurements for 1I. The ^{1}H NMR spectrum of **1I** in D_2O initially shows two different Cp^* signals (see Figure S4.), integrating for 15 protons. The intensity of one Cp^* resonance

increases up to a plateau while the other disappears with time (Figure S4). This suggests that **1I** undergoes two independent reactions: H/D exchange and irreversible coordination of I^- to the metal centre, affording $[Cp^*Rh(I)(PTA)_2]Cl$. The latter does not undergo H/D exchange, probably because the dissociation of Rh-I bond occurs more difficultly. Both the processes were considered to extract the rate of H/D exchange of **1**I.

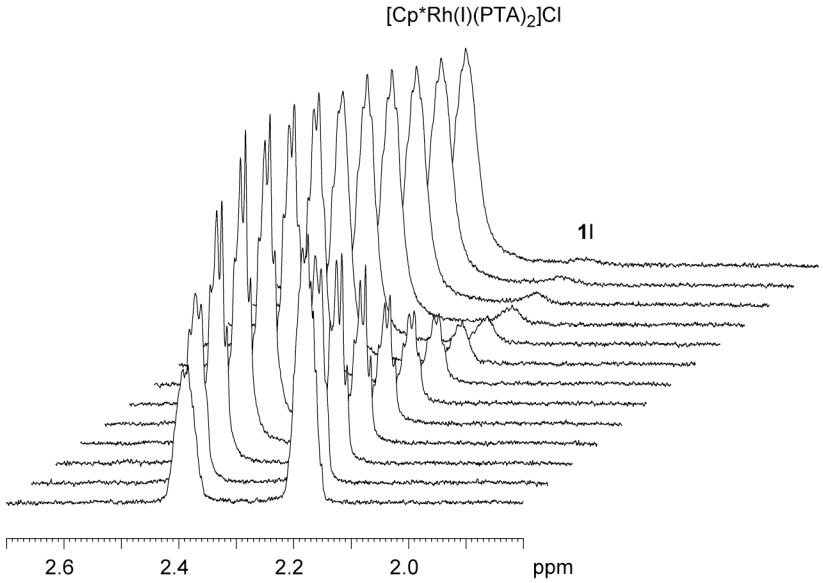

Figure S4. A stack plot of a series of ^1H spectra for **1I** (T = 343 K, C = 5 mM), showing the deuteration of the Cp^* in **1I** and the simultaneous formation of $[Cp^*Rh(I)(PTA)_2]Cl$.

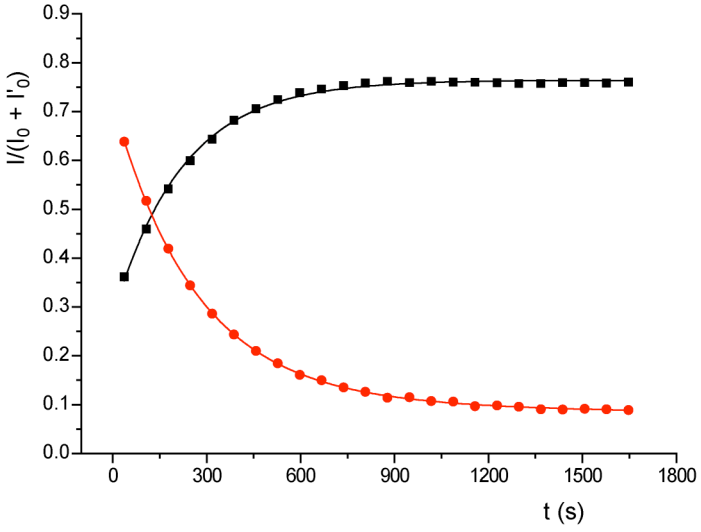

Figure S5. Plot of the $I/(I_0 + I'_0)$ ratio (I = intensity of the Cp* signal, I_0 and I_0' = intensity of the Cp^* signal at time = 0) *vs*. time, relative to Figure S4. The black squares refer to the intensity of the signal relative to $[Cp^*Rh(I)(PTA)_2]Cl$, the red circles to the intensity of the **1I** signal. The black best fit is a monoexponential equation: $I/I_0 = (-0.485 \pm 0.006)*\exp[-(45 \pm 1)*10^{-4}*t] + (0.764 \pm 0.001)$, $r^2 = 0.9976$. The red best fit is a biexponential decay: $I/I_0 = (0.045 \pm 0.009)*\exp[-(43 \pm 2)*10^{-4}*t] + (0.61 \pm 0.03)*\exp[-(4.3 \pm 0.2)*10^{-4}*t] + (0.06 \pm 0.01)$, $r^2 = 0.9998$.

Particularly, kinetics of $[Cp^*Rh(I)(PTA)_2]Cl$ formation were obtained by fitting the Cp^* intensity with a monoexponential equation ($k_1 = 45 *10^{-4}\ s^{-1}$). On the contrary, fitting the decrease of the Cp^* signal intensity of **1I** with a biexponential equation afforded the kinetic parameters for both the H/D exchange ($k_1 = 43 *10^{-4}\ s^{-1}$) and the irreversible formation of $[Cp^*Rh(I)(PTA)_2]Cl$ ($k_2 = 4.3*10^{-4}\ s^{-1}$). Coherently, k_1 obtained by the two methods are equal within the experimental error.

Computational Details. Calculations were performed with the Gaussian03 software package[11] at the DFT/B3LYP level. Core electrons of rhodium were described using the LANL2DZ pseudo potential and their valence electrons were expressed through a LANL2DZ basis set.[12] All the remaining atoms were described with a 6-31g* basis set. Solvent effects were introduced by means of the Polarizable Continuum Model (PCM),[13] using standard UFF solvation spheres. The free energies of solvation were computed in water ($\varepsilon = 78.2$), starting from the gas-phase optimized geometries. For the transition state analytical frequencies were calculated, in order to check that only one imaginary value is obtained.

Coordinates. Optimised geometries (xyz coordinates plus related absolute internal and Gibbs energies, in the gas-phase and in water).

E(gas): gas phase internal energy

E(PCM): gas phase internal energy + contribution of the Gibbs energy of solvation coming from the continuum model

G(gas): gas phase Gibbs energy, obtained adding zero-point, thermal and entropy corrections to the

internal energy

G_{water} = G(gas) + [E(PCM)-E(gas)]: gas phase Gibbs energy + contribution of the Gibbs energy of solvation coming from the continuum model.

$1^{+}(H_2O)_3$

E(gas) = -2671.409397 ha

E (PCM) = -2671.489144 ha

G(gas) = -2670.792018 ha

G_{water} = -2670.871764 ha

Rh	-0.485	-1.729	-0.422
Cl	0.110	-0.520	-2.527
P	1.542	-0.735	0.522
N	4.281	-1.043	1.158
C	3.149	-1.839	0.673
H	3.371	-2.252	-0.314
H	2.959	-2.657	1.368
P	-1.935	0.160	0.193
N	3.035	0.564	2.533
C	1.679	0.056	2.301
H	0.959	0.872	2.376
H	1.430	-0.704	3.047
N	3.648	1.142	0.212
C	2.391	0.711	-0.449
H	1.683	1.542	-0.538
H	2.605	0.346	-1.455
N	-3.756	2.054	-0.834
C	4.068	-0.501	2.524
H	5.010	-0.075	2.878
H	3.771	-1.307	3.198
N	-4.366	1.058	1.336
C	4.673	0.049	0.246
H	5.617	0.473	0.598
H	4.811	-0.341	-0.765
N	-2.557	2.715	1.207
C	3.421	1.650	1.608
H	2.646	2.418	1.583
H	4.353	2.097	1.961
C	-2.836	1.023	-1.314
H	-2.062	1.461	-1.941
H	-3.371	0.258	-1.883
C	-3.545	-0.155	1.262
H	-3.244	-0.461	2.268
H	-4.124	-0.959	0.805
C	-1.410	1.817	1.116
H	-1.058	1.560	2.119
H	-0.627	2.266	0.499
C	-3.056	3.160	-0.125
H	-3.764	3.978	0.027
H	-2.213	3.500	-0.727
C	-4.852	1.520	0.005
H	-5.584	2.314	0.171
H	-5.343	0.691	-0.512
C	-3.673	2.182	2.019
H	-4.400	2.982	2.183
H	-3.297	1.844	2.988
C	-1.479	-3.494	0.619
C	-0.120	-3.899	0.321
C	0.065	-3.850	-1.108
C	-1.224	-3.520	-1.706
C	-2.173	-3.308	-0.653
H	0.148	2.091	-2.103
O	0.131	2.734	-1.367
H	0.760	3.513	-1.559
H	2.858	4.184	-1.554
O	1.928	4.509	-1.767
H	1.864	5.474	-1.830
H	5.043	3.570	-1.608
O	4.203	3.458	-1.134
H	4.120	2.565	-0.678
C	1.276	-4.251	-1.893
H	2.171	-4.307	-1.266
H	1.471	-3.539	-2.701
H	1.135	-5.240	-2.349
C	0.842	-4.438	1.335
H	1.850	-4.542	0.932
H	0.514	-5.439	1.648
H	0.885	-3.821	2.238
C	-2.114	-3.576	1.975
H	-1.426	-3.262	2.764
H	-2.412	-4.611	2.194
H	-3.012	-2.959	2.048

C	-3.652	-3.150	-0.850	C	-4.594	-1.193	-1.513	H	-3.411	-0.305	1.561
H	-3.897	-2.354	-1.559	C	-2.778	-2.738	-1.988	H	2.109	0.009	-2.828
H	-4.170	-2.947	0.088	C	-2.400	-0.316	-2.215	H	1.147	-1.298	-2.106
H	-4.073	-4.081	-1.254	C	3.611	1.123	-0.269	H	2.257	-3.042	-0.794
C	-1.505	-3.499	-3.172	C	2.060	-0.993	0.909	H	4.030	-3.138	-0.837
H	-0.781	-2.878	-3.707	C	2.022	-0.658	-1.967	H	5.332	-1.330	-1.832
H	-2.502	-3.110	-3.388	C	4.473	-0.663	-1.730	H	4.504	0.073	-2.535
H	-1.446	-4.518	-3.579	C	3.179	-2.461	-0.733	H	5.374	-1.637	0.580
				C	4.513	-0.973	0.679	H	4.564	-0.469	1.647
$1^{++'}(H_2O)_2$				N	-2.488	-2.860	-0.535	H	3.754	1.847	-1.073
E(gas) = -2210.897689 ha				N	-3.359	-1.410	-2.313	H	3.747	1.621	0.693
E (PCM) = -2211.108062 ha				N	-4.324	-1.306	-0.055	H	2.157	-0.546	1.899
G(gas) = -2210.278509 ha				N	3.229	-1.468	-1.828	H	1.187	-1.644	0.914
G_{water} = -2210.488882 ha				N	3.264	-1.805	0.618	O	-0.132	0.684	2.310
				N	4.552	0.020	-0.414	H	-0.020	1.291	3.059
Rh	-0.258	1.681	0.333	H	-0.476	-2.288	-0.674	H	-0.101	-0.313	2.619
P	1.762	0.428	-0.348	H	-1.163	-2.197	0.969	H	0.863	-2.260	3.086
P	-1.775	-0.129	-0.361	H	-1.863	-2.894	-2.564	O	0.007	-1.696	3.128
C	-1.725	3.372	-0.299	H	-3.500	-3.509	-2.264	H	-0.625	-2.037	3.783
C	-1.374	3.551	1.077	H	-4.456	-3.407	-0.024	H	2.489	-3.769	3.462
C	0.072	3.814	1.147	H	-3.519	-2.712	1.314	O	2.175	-3.051	2.890
C	0.595	3.778	-0.182	H	-5.013	-0.209	-1.737	H	2.793	-2.851	2.133
C	-0.493	3.389	-1.083	H	-5.324	-1.955	-1.791	C	-2.318	3.639	2.235
C	-1.369	-2.042	-0.093	H	-1.534	-0.506	-2.855	H	-1.885	3.228	3.151
C	-3.554	-0.193	0.483	H	-2.865	0.623	-2.524	H	-3.254	3.111	2.041
C	-3.733	-2.635	0.246	H	-4.066	0.751	0.287	H	-2.568	4.688	2.442

C	-3.109	3.334	-0.863	C	-1.525	3.428	-0.655	H	-4.528	-3.321	0.419
H	-3.177	2.731	-1.772	C	-1.502	3.405	0.811	H	-3.429	-2.613	1.622
H	-3.407	4.355	-1.139	C	-0.152	3.733	1.238	H	-5.248	-0.147	-1.275
H	-3.846	2.974	-0.143	C	0.668	3.822	0.067	H	-5.581	-1.890	-1.262
C	-0.421	3.399	-2.579	C	-0.189	3.635	-1.114	H	-1.924	-0.503	-2.782
H	0.556	3.076	-2.946	C	-1.457	-1.988	-0.040	H	-3.193	0.648	-2.318
H	-0.591	4.416	-2.961	C	-3.531	-0.110	0.749	H	-4.053	0.836	0.592
H	-1.179	2.753	-3.030	C	-3.769	-2.554	0.586	H	-3.275	-0.195	1.809
C	1.964	4.201	-0.610	C	-4.816	-1.132	-1.084	H	2.028	-0.303	-3.047
H	2.286	3.696	-1.524	C	-3.088	-2.705	-1.741	H	1.122	-1.553	-2.181
H	2.715	4.039	0.166	C	-2.707	-0.292	-2.048	H	2.320	-3.147	-0.779
H	1.955	5.278	-0.828	C	3.528	1.084	-0.668	H	4.109	-3.198	-0.860
C	0.812	4.207	2.387	C	2.074	-0.923	0.764	H	5.325	-1.454	-2.038
H	1.882	3.997	2.315	C	1.977	-0.875	-2.119	H	4.428	-0.152	-2.843
H	0.422	3.704	3.278	C	4.448	-0.807	-1.972	H	5.461	-1.496	0.389
H	0.702	5.285	2.567	C	3.232	-2.548	-0.827	H	4.629	-0.235	1.354
				C	4.599	-0.826	0.437	H	3.635	1.731	-1.541
A1				N	-2.626	-2.816	-0.332	H	3.681	1.686	0.231
E(gas) = -2210.8864491 ha				N	-3.686	-1.377	-2.020	H	2.150	-0.358	1.694
E (PCM) = -2211.08589 ha				N	-4.378	-1.225	0.333	H	1.235	-1.609	0.867
G(gas) = -2210.245401 ha				N	3.222	-1.643	-1.943	O	0.328	0.863	1.977
G_{water} = -2210.466800 ha				N	4.527	0.004	-0.733	H	-0.073	0.004	2.241
				H	-0.645	-2.253	-0.726	H	0.960	-2.354	3.114
Rh	-0.229	1.688	0.154	H	-1.123	-2.138	0.991	O	0.067	-1.975	2.964
P	1.721	0.350	-0.620	H	-2.249	-2.881	-2.420	H	-0.496	-2.118	3.748
P	-1.865	-0.082	-0.286	H	-3.846	-3.471	-1.918	H	3.349	-2.993	3.728

O	2.847	-3.211	2.917
H	2.674	-4.174	2.900
C	-2.690	3.383	1.722
H	-2.479	2.827	2.640
H	-3.570	2.944	1.248
H	-2.960	4.408	2.013
C	-2.757	3.406	-1.506
H	-2.557	3.028	-2.512
H	-3.146	4.427	-1.615
H	-3.558	2.808	-1.062
C	0.237	3.848	-2.536
H	1.281	3.565	-2.699
H	0.145	4.908	-2.807
H	-0.380	3.280	-3.238
C	2.094	4.281	0.038
H	2.617	3.958	-0.865
H	2.654	3.938	0.912
H	2.128	5.379	0.046
C	0.300	3.817	2.655
H	1.230	4.382	2.755
H	0.463	2.791	3.028
H	-0.455	4.294	3.286
N	3.328	-1.745	0.523
H	3.396	-2.399	1.334

TS

E(gas) = -2210.848008 ha

E (PCM) = -2211.069503 ha

G(gas) = -2210.230188 ha

G_{water} = -2210.451683 ha

Rh	1.829	1.908	3.238
C	3.694	0.425	3.540
C	3.731	1.179	2.280
C	2.626	0.739	1.442
C	1.813	-0.157	2.223
C	2.420	-0.285	3.538
C	4.510	0.675	4.676
H	5.510	1.062	4.485
H	4.483	-0.065	5.474
C	4.921	1.974	1.834
H	5.758	1.297	1.613
H	5.262	2.664	2.612
H	4.724	2.548	0.927
C	2.464	1.012	-0.022
H	2.981	0.238	-0.606
H	2.897	1.972	-0.313
H	1.414	1.002	-0.327
C	0.652	-0.949	1.703
H	1.011	-1.870	1.222
H	0.081	-0.394	0.954

H	-0.033	-1.252	2.499
C	2.002	-1.239	4.617
H	2.645	-2.129	4.604
H	0.974	-1.588	4.487
H	2.099	-0.791	5.612
P	-0.279	2.041	4.461
P	1.581	4.122	2.220
C	1.065	5.666	3.306
C	3.092	5.012	1.339
C	2.289	7.270	1.898
C	1.646	6.255	-0.215
C	-0.049	6.805	1.430
C	0.294	4.452	0.782
C	-1.141	0.507	5.302
C	0.101	2.963	6.097
C	-1.936	2.988	4.066
C	-3.273	1.701	5.704
C	-2.291	3.807	6.354
C	-1.600	1.621	7.441
N	0.983	6.884	2.501
N	0.334	5.852	0.358
N	2.699	6.323	0.832
N	-2.805	3.036	5.256
N	-2.140	0.948	6.293
H	0.087	5.462	3.754
H	1.794	5.781	4.114

H	-1.007	6.505	1.864	O	0.486	4.604	8.865	H	4.631	2.528	0.796
H	-0.160	7.797	0.987	H	0.204	5.503	9.127	C	2.343	0.947	-0.011
H	2.186	8.264	1.459	O	2.820	2.565	5.062	H	2.762	0.123	-0.604
H	3.057	7.306	2.675	H	2.836	3.437	5.534	H	2.816	1.867	-0.364
H	1.943	5.548	-0.993	H	3.793	1.737	5.114	H	1.274	1.002	-0.239
H	1.539	7.245	-0.663	N	-1.089	3.052	7.036	C	0.646	-1.000	1.822
H	-0.706	4.194	1.141	H	-0.755	3.582	7.870	H	0.991	-1.895	1.287
H	0.539	3.794	-0.056					H	0.013	-0.433	1.134
H	3.428	4.381	0.513	**A2**				H	0.027	-1.346	2.654
H	3.905	5.106	2.063	E(gas) = -2210.866146 ha				C	2.105	-1.193	4.694
H	-2.456	2.474	3.254	E (PCM) = -2211.088568 ha				H	2.765	-2.072	4.703
H	-1.703	4.003	3.734	G(gas) = -2210.246586 ha				H	1.080	-1.564	4.613
H	-1.914	4.778	6.030	G_{water} = -2210.469008 ha				H	2.223	-0.697	5.664
H	-3.050	3.935	7.130					P	-0.290	2.044	4.432
H	-4.057	1.825	6.455	Rh	1.801	1.890	3.176	P	1.608	4.138	2.229
H	-3.684	1.150	4.858	C	3.811	0.356	3.458	C	1.090	5.671	3.330
H	-2.368	1.773	8.202	C	3.717	1.174	2.220	C	3.114	5.047	1.357
H	-0.749	1.085	7.865	C	2.592	0.709	1.447	C	2.308	7.297	1.943
H	-1.631	-0.095	4.535	C	1.824	-0.198	2.287	C	1.667	6.309	-0.182
H	-0.376	-0.103	5.786	C	2.475	-0.281	3.563	C	-0.029	6.833	1.470
H	0.920	2.438	6.589	C	4.825	0.320	4.360	C	0.322	4.492	0.795
H	0.445	3.976	5.884	H	5.764	0.831	4.178	C	-1.139	0.515	5.294
H	1.959	4.849	7.463	H	4.779	-0.313	5.239	C	0.044	3.002	6.063
O	2.492	4.918	6.641	C	4.875	1.974	1.704	C	-1.958	2.956	4.003
H	3.216	5.561	6.753	H	5.709	1.302	1.458	C	-3.300	1.674	5.643
H	0.896	4.164	9.637	H	5.245	2.684	2.451	C	-2.370	3.810	6.268

C	-1.654	1.655	7.406	H	-1.608	-0.111	4.531
N	1.003	6.903	2.543	H	-0.371	-0.074	5.799
N	0.356	5.896	0.387	H	0.857	2.495	6.583
N	2.719	6.365	0.866	H	0.375	4.016	5.835
N	-2.848	3.009	5.179	H	1.940	4.811	7.554
N	-2.162	0.954	6.263	O	2.595	4.812	6.819
H	0.113	5.459	3.778	H	3.268	5.504	6.944
H	1.822	5.781	4.136	H	0.784	4.263	9.631
H	-0.986	6.526	1.900	O	0.446	4.691	8.819
H	-0.143	7.831	1.040	H	0.156	5.600	9.040
H	2.202	8.297	1.516	O	2.818	2.575	5.344
H	3.076	7.326	2.720	H	2.891	3.432	5.850
H	1.965	5.612	-0.968	H	3.656	2.064	5.297
H	1.557	7.304	-0.618	N	-1.162	3.092	6.982
H	-0.678	4.225	1.150	H	-0.852	3.638	7.812
H	0.569	3.844	-0.051				
H	3.451	4.428	0.524	**Chloride**			
H	3.930	5.137	2.079	E(gas) = -460.248702 ha			
H	-2.457	2.421	3.192	E (PCM) = -460.373669 ha			
H	-1.738	3.970	3.659	G(gas) = -460.263705 ha			
H	-2.008	4.783	5.932	G_{water} = -460.388701 ha			
H	-3.142	3.936	7.031				
H	-4.097	1.796	6.379				
H	-3.686	1.101	4.800				
H	-2.437	1.809	8.152				
H	-0.799	1.144	7.852				

[1] D. D.Perrin and W. Armarego, *Purification of Laboratory Chemicals*, 3a ed.l Butterworth and Heinemann, Oxford, 1988.

[2] (a) D. J. Daigle, A. B. Pepperman and G. Boudreaux, *J. Heterocycl.Chem.* 1974, **11**, 1085; (b) D. J. Daigle, *Inorg. Synth.* 1998, **32,** 40.

[3] K. J. Coskran and J. G. Verkade, *Inorg. Chem.* 1965, **11**, 1655.

[4] J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.* 1969, **91**, 5970.

[5] A. Dorcier, W. Han Ang, S. Bolaño, L. Gonsalvi, L. Juillerat-Jeannerat, G. Laurenczy, M. Peruzzini, A. D. Phillips, F. Zanobini and P. J. Dyson, *Organometallics* 2006, **25**, 4090.

[6] M. S. Eisen, A. Haskel, H. Chen, M. M. Olmstead, D. P. Smith, M. F. Maestre and R. H. Fish, *Organometallics* 1995,**14**, 2806.

[7] M. Erlandsson, V. R. Landaeta, L. Gonsalvi, M. Peruzzini, A. D. Phillips, P. J. Dyson and G. Laurenczy,. *Eur. J. Inorg. Chem.* 2008, **4**, 620-627.

[8] D. N. Akbayeva, L. Gonsalvi, W. Oberhauser, M. Peruzzini, F. Vizza, P. Brüggeller, A. Romerosa, G. Sava and A. Bergamo, *Chem. Commun.* 2003, 264.

[9] S. Bolaño, M. Plaza, J. Bravo, J. Castro, M. Peruzzini, L. Gonsalvi, G. Ciancaleoni and A. Macchioni, *Inorg. Chim. Acta*, 2009, doi: 10.1016/j.ica.2009.05.041.

[10] K. Mikkelsen and S. O. Nielsen, *J. Phys. Chem.*, 1960, **64**, 632.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr.; T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain,

O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2004.

[12] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270.

[13] M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.* 1996, **255**, 327.